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Review Article

Distribution of rare earth elements of Tunisian margin clays

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Abstract

The rare earth element (*REE*) content of the Tunisian Permian–Neogene shales have been studied to determine the origins of the clay minerals in these shales. The Permian–Neogene series overlies the Palaeozoic basement that has been studied *via* oil-drilling cores. This study of *REE*s was performed in various palaeogeographical domains of Tunisia, from the 'Saharan Platform' in the south to the 'Nappes Zone' in the north. In this work, those levels rich in illite (Palaeozoic, Triassic and Jurassic), smectite (Campanian–Maastrichtian) and palygorskite (continental Eocene) as well as some Miocene levels rich in halloysite are examined. The distribution of *REE*s in the Tunisian margin sediments is generally homogeneous, except for the Miocene levels containing halloysites. The normalization curves of *REE*s *vs* North American shale composite characterize the inherited clays regardless of the dominant minerals, except for a few cases of neoformation. The flat *REE* curves indicate a detrital origin of the studied clay levels.

Keywords: clay, climate, eustatism, *REE*s, tectonic, Tunisia

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This study aims to identify the rare earth element (*REE*) contents in some levels of the stratigraphic Permian–Neogene sequences in Tunisia that overlie the Palaeozoic basement that has been studied *via* oil-drilling cores (Jamoussi, 2001).

The clay fraction of the examined series is dominated by illite in the Palaeozoic, Triassic and Jurassic, by smectite in the Campanian–Maastrichtian, by palygorskite in the continental Eocene and by halloysites in the Miocene (Jamoussi, 2001; Jamoussi *et al.*, 2001, 2003). The study field extends from the 'Saharan Platform' in the south to the 'Nappes Zone' in the north (Fig. 1). Most of these clay minerals have a detrital origin, with some cases of neoformation for palygorskites (Jamoussi *et al.*, 2003). The mineralogical variation of the clays in the studied stratigraphic series is the result of the geodynamic history of the basins (Jamoussi, 2001; Jamoussi *et al.*, 2003). Moreover, the distribution of trace elements is approximately similar in the various investigated levels, reflecting a common origin of the clay minerals.

The *REE*s were studied to specify the origins of the clay minerals and to determine the distribution of lanthanides according to the age of the stratigraphic series and their mineralogical composition along the examined domains. The aim of this work is to describe the chemical composition of the clay minerals in the Palaeozoic, Mesozoic and Cenozoic sequences of the Tunisian margin.

Geological setting

The region examined extends from the 'Saharan Platform' in the south, through the Southern, Central, Eastern and Northern Atlas to the 'Nappes Zone' (Fig. 1). The stratigraphic succession spreads from the Permian to the Quaternary series. The Palaeozoic rocks of the 'Saharan Platform' were investigated using core-drilling samples obtained from hydrocarbon exploration companies (Jamoussi, 2001; Jamoussi *et al.*, 2003).

The 'Saharan Platform' is made up essentially of granitic and metamorphic Precambrian basement rocks covered by Palaeozoic clay–sandstone sub-tabular series (Busson, 1967; Memmi *et al.*, 1986; Bouaziz, 1995). The Southern Atlas includes two major fold chains with a Cretaceous core and, sometimes, with a Jurassic core. More precisely, the 'Northern Chotts Chain' in the south and the 'Gafsa Chain' in the north are separated by vast plains with continental Neogene filling. These chains originated in the Late Cretaceous from a strike-slip tectonic movement (Zargouni, 1985; Boukadi, 1994; Bédir, 1995). The Central Atlas has formed by a succession of north-east to south-west and east to west folded drive structures (Burollet, 1956; Ben Ayed, 1986; M'Rabet, 1987; Bédir, 1995). The Eastern Atlas is limited to the west and north-west by the north to south fault called the 'N–S Axis' corridor and the Tunisian ridge of Zaghouan (Turki, 1985). These structures are separated by syncline gutters with significant accumulations of Neogene sediments and subsident platforms (Colleuil, 1976; Ben Salem, 1992; Bédir, 1995). The Northern Atlas consists of north-east to south-west direction anticlines pouring southwards and arranged in overlapping scales. It is limited to the north by large Triassic structures called the 'Diapirs Zone'. This area is also characterized by the presence of transverse north-west to south-east management collapse ditches (Solignac, 1927; Crampon, 1973; Rouvier, 1977; Perthuisot, 1978; Ben Ayed, 1986).

The Numidian 'Nappes Zone' is made up of turbiditic clay–sandstone sedimentary units (Mahersi, 1991) of Oligo-Miocene age in an allochthonous position (Rouvier, 1977). The Numidian 'Nappes Zone' was thrust southwards from the Serravallian (Tlig *et al.*, 1991).

Three phosphate samples of Palaeocene–Eocene age were added to this work based on the study conducted by Garnit *et al.* (2017).

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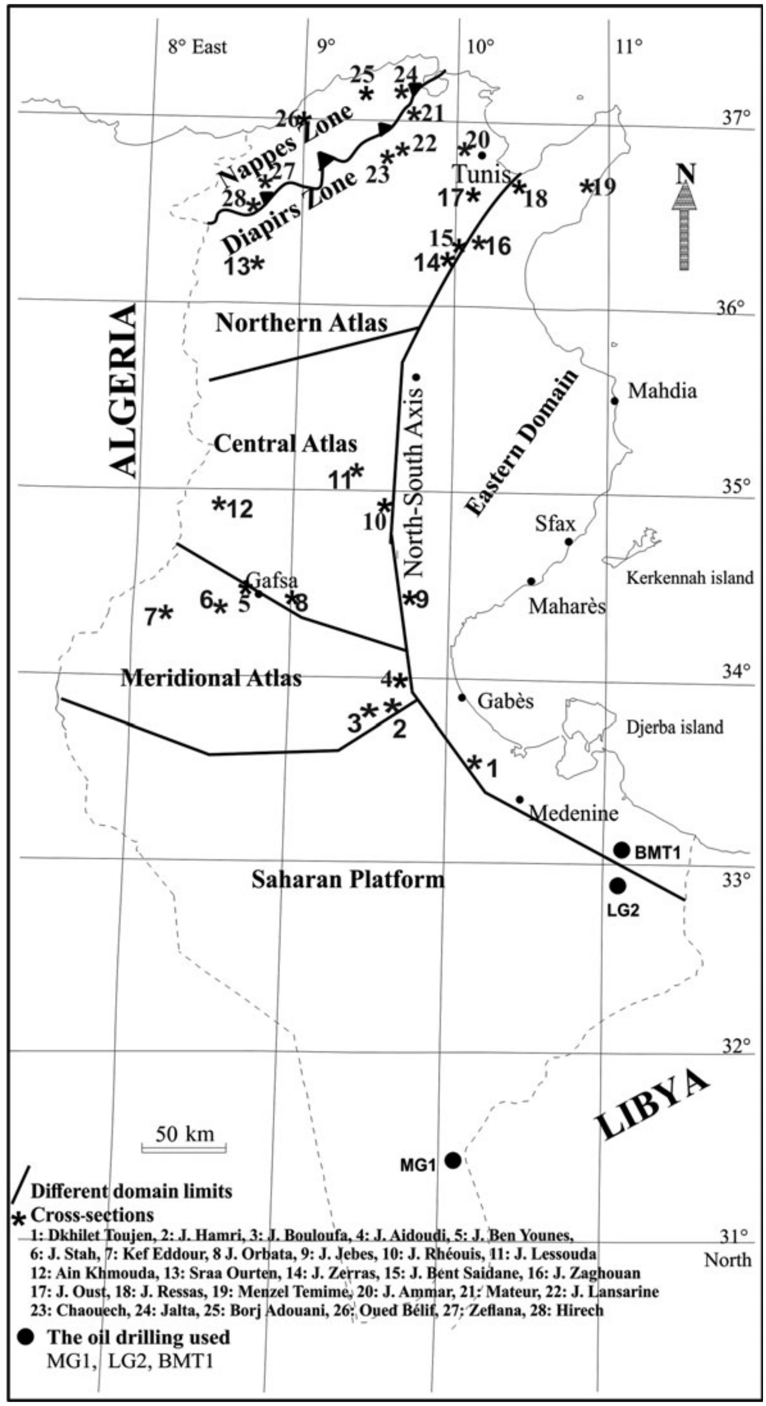

Fig. 1. Locations of the cross-sections and petroleum wells studied.

A sample of rhyodacite, taken from among the rare volcanic points in the northern Tunisian late Miocene (Serravallian–Messinian) magmatic rocks belonging to the post-collisional magmatism of the Mediterranean Maghreb margin in Oued Bélif, was obtained as a reference according to Decrée *et al.* (2014).

Materials and methods

The clay samples studied, collected from several geological cross-sections (Fig. 1), are representative of the lithostratigraphic sequences that crop out in the various geological domains studied. The qualitative and semi-quantitative mineralogical compositions, corresponding to the bulk rock and clay fraction, were identified and estimated using X-ray diffraction (XRD) with a Siemens Kristalloflex 810 diffractometer and Cu-$K\alpha$ radiation on either random powder for bulk rock or oriented clay-size particles under the following conditions: air dried, saturated with ethylene glycol and heated at 550°C. The clay minerals were quantified using the classic method that measures peak areas and takes into account the corresponding reflective powers. The abbreviations of the clay minerals and associated minerals follow the recommendations and listing of Warr (2020).

Chemical analyses of major elements were carried out using a Perkin-Elmer atomic absorption spectrophotometer. Trace

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elements and *REE*s were determined using inductively coupled plasma mass spectrometry (Perkin-Elmer SCIEX Elan-5000 ICP-MS spectrometer) with Rh and Re as internal standards. The accuracy levels were 2 and 5% for elemental concentrations of 50 and 5 ppm, respectively. The detection limits of the elements were 100 ppb for *REE*s and Th, 5 ppm for transition elements and Cs, Rb, Sr, Ba and Pb and 10 ppm for Li.

Distribution diagrams were smoothed by normalizing *REE* abundance relative to North American shale composite (NASC; Haskin *et al.*, 1966, 1968; Haskin & Paster, 1979; Gromet *et al.*, 1984; Jamoussi, 2001).

Geochemical evolution of the *REE*s in the study areas

Thirty-nine clay samples, three phosphate samples and one rhyodacite sample from the various palaeogeographical domains of Tunisia were studied in the present work (Fig. 1). The geochemistry of the major elements shows an abundance of SiO_2 and Al_2O_3 in the clay samples. The clays are slightly ferriferous. The Al_2O_3 correlates well with Fe_2O_3, K_2O and Na_2O (Table 1), indicating that these elements are present in the detrital phyllosilicate phases of the examined samples (Jamoussi, 2001). The highest concentrations of Al_2O_3 were observed in the halloysites of Tamra and Ain Khmouda (Table 1).

The clay fraction is dominated by illites in the Palaeozoic, Triassic and Jurassic sediments, smectite in the Campanian–Maastrichtian sediments, palygorskite in the continental Eocene and halloysite at some levels of the Miocene (Fig. 2 & Table 2).

There is a cause/effect relationship between the mineralogical composition of the sediments and the geodynamic history of the basins (Fig. 2). Smectites are present and often abundant during periods with high sea levels, whereas palygorskite confirms the continental character of the deposits.

The distribution of trace elements is similar in the various studied levels (Fig. 3 & Table 3), reflecting the common history, origin and evolution of these various clay types and proving the presence of inherited minerals, except for halloysites, palygorskites and sepiolites.

Some samples are relatively rich in trace elements (Fig. 3 & Table 3), in most cases due to their proximity to zones where lead mineralization mainly occurs. The maximum trace element contents were detected in the illitic Triassic clays of J. Ammar (TAM2), followed by the illitic Jurassic clays of J. Ressas (RC4; Fig. 3 & Table 3), generally because of their proximity to the mineralization zones. Relatively high abundances of trace elements were also observed in the Kef Eddour phosphates (KCEI) and in the samples of rhyodacite from Oued Bélif (AOr4).

Clay minerals are among the main sediment fractions involved in *REE* transport. The latter are reliable tracers that help with determining the origins of rocks because of their limited surface mobility (Wronckiewiez & Condie, 1990). The normalization curves of the *REE*s with respect to NASC (Fig. 4 & Table 4) show a more regular distribution compared to those of the detrital clays from the continental environments. The *REE* diagrams are comparable across the studied clay levels, indicating the inherited origin of these clays, except for the palygorskite clays, which were partly neoformed (Jamoussi, 2001; Jamoussi *et al.*, 2003). The flat patterns of the *REE*/NASC curves confirm the detrital origin of the clay levels examined (Wray, 1995). The spectra also tend to become depleted of heavy *REE*s (Fig. 4).

The negative Ce anomaly (characteristic of seawater), which affects the minerals formed in a marine environment (Piper, 1974; Courtois & Hoffert, 1977; De Baar *et al.*, 1988; Murray *et al.*, 1990), is very weak or absent, even in levels where the clay fraction is very rich in smectite, except for the phosphate-rich levels, confirming their marine origin.

One can observe a slight fractionation with impoverishment of heavy *REE*s compared to light REEs. This fractionation could result from the complexation of *REE*s with organic matter. This mechanism favours the maintenance of the heaviest elements in solution, which are thus depleted in the solid phase (Courtois & Chamley, 1978; Nesbitt, 1979).

The mobility and fractionation of *REE*s at the rock–fluid interface are very low (MacLennan *et al.*, 1980; Taylor & MacLennan, 1985; MacLennan, 1989). As a result, these elements move from the weathering profiles to the sedimentation basins without being involved in chemical processes during transport (Fleet, 1984). The behaviour of *REE*s during continental alterations is therefore governed by the parent-rock composition. Consequently, it may be concluded that the detrital clays transported to the sedimentation basins retain their detrital imprints (Bonnot-Courtois, 1981; Fleet, 1984; Setti *et al.*, 2004). The distribution of *REE*s is thus related directly to that of the parent rock (Cullers *et al.*, 1975). These elements are adsorbed by the existing minerals, which leads to great *REE* levels in detrital minerals. The very low concentrations of *REE*s in sedimentation ponds lead to low levels of *REE*s in the neoformed minerals from these solutions. Once adsorbed on the clays, *REE*s form complexes that are linked strongly to the clayey network (Leleyter *et al.*, 1999).

The *REE*s located in an interlayer position or in exchangeable sites are among the chemical elements that are related most closely to detrital phyllosilicates. Their adsorption onto the clays occurs easily, while their desorption is relatively difficult. The high charge of these elements should stabilize them in the exchangeable sites of clay minerals (Bonnot-Courtois, 1981; Bonnot-Courtois & Jaffrezic-Renault, 1982). *REE*s are therefore relatively immobile and their concentrations are great in detrital phyllosilicates and low in natural solutions. The few previous works carried out in Tunisia on *REE*s concerned mainly the phosphatic series (Ounis *et al.*, 2008; Garnit *et al.*, 2012, 2017; Bouabdallah *et al.*, 2019) and the Oued Bélif belt breccia (Decrée *et al.*, 2013, 2014). Hence, it is important to conduct further studies in an attempt to separate these *REE*s from the gangue for possible exploitation.

Tlig & Steinberg (1980) showed that the *REE* spectra of the Late Jurassic and lower Cretaceous clays of southern Tunisia are comparable to those of the Callovian clays and show a slight depletion of heavy *REE*s. These authors concluded that these *REE*s have an inherited origin. The relatively great *REE* concentrations in the phosphate pellets of the Gafsa phosphate basin correlate with the porosity and specific surface area of the cryptocrystalline apatite and the palaeo-depositional environment (Ounis *et al.*, 2008; Galfati *et al.*, 2010; Garnit *et al.*, 2012, 2017). Finally, the Oued Bélif breccia in the north-west of Tunisia is enriched in *REE*s (Decrée *et al.*, 2013, 2014).

Distribution of *REE*s according to clay mineralogy

The data present above suggest that the distribution of *REE*s in the Tunisian sediments has changed slightly over time. The abundances of *REE*s vary considerably depending on the nature of the clay minerals, especially at the lowest *REE*-rich levels (Tables 2 & 4). In accordance with Torres-Ruiz *et al.* (1994), the present study showed that the *REE* contents in the clay minerals obtained by

Table 1. Chemical analysis of the major elements (wt.%) from the levels studied.

Age	Site	Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2	MnO	LOI	Total
Miocene	Oued Bélif	OAr4[a]	68.75	15.5	2.8	0.8	1.02	0.91	7.93		0.39	0.01	1.91	100.02
Pliocene	Menzel Temime	CBL	47.85	20.51	7.74	1.67	2.18	0.23	2.84		0.88	0.03	13.90	97.83
Miocene	Aïn Khmouda	AK9	38.90	35.55	0.29	0.42	0.16	0.73	0.36	0.49		0.01	22.13	99.04
	Tamra	HT	42.01	31.65	1.86	0.14	0.08	0.67	0.12	0.43		0.01	16.55	93.52
Eocene	J. Lessouda	JLS3	28.95	9.88	3.79	12.75	13.47	0.12	2.51	0.43		0.05	27.90	99.85
	J. Rhéouis	JRHA6	29.24	5.10	2.36	14.25	14.10	0.39	0.81	1.04		0.03	31.76	99.08
	J. Rhéouis	JRH2	21.39	4.91	2.54	19.50	14.51	0.23	1.47	0.37		0.03	34.12	99.07
	J. Rhéouis	JRH6	22.46	4.91	2.50	18.80	14.51	0.20	1.26	0.39		0.03	34.11	99.17
	J. Bouloufa	BOL5	39.87	4.16	1.45	22.50	1.19	0.43	1.69	0.37		0.02	28.36	100.04
	J. Hamri	HM3	32.89	2.08	0.63	31.80	1.54	0.36	1.04	0.59		0.02	28.55	99.50
Palaeocene–Eocene	Sraa Ouertene	SRO1[b]	21.37	3.41	1.06	38.93	0.64	0.54	0.91	0.69	0.17	0.01	25.09	92.82
	J. Jeebs	JBS4[b]	31.47	2.11	0.69	24.79	7.88	0.70	1.47			0.01	19.64	88.76
	Kef Eddour	KCEl[b]	6.97	1.28	0.56	45.88	0.62	1.42	0.32	3.90	0.05	0.00	11.90	72.91
Campanian–Maastrichtian	J. Orbata	K34	46.06	19.03	5.72	2.28	2.07	1.37	1.35	3.92			17.84	99.64
	J. Stah	T23	36.93	19.94	5.72	9.92	1.46	3.30	1.38	0.94			19.25	98.84
	J. Stah	T24	53.26	14.38	6.15	3.78	2.16	1.36	1.56	0.27			16.97	99.89
Campanian	Chaouech	GL9	24.19	10.08	4.58	28.00	1.49	0.46	0.84	1.14		0.01	28.49	99.28
	Chaouech	GL11	22.10	10.38	4.00	30.10	1.06	0.13	0.84	0.27		0.01	30.52	99.41
	J. Orbata	K19	28.88	11.71	3.15	24.50	1.33	0.24	0.77				28.63	99.21
Coniacian–Santonian	O. Louh Zeflana	Z8	30.09	12.03	3.86	26.10	0.53	0.13	0.84	0.32		0.01	25.73	99.64
	J. Oust	M4	23.83	8.88	3.57	28.70	1.06	0.19	2.54	0.27		0.05	29.96	99.05
	J. Stah	T6	19.40	10.27	3.82	27.95	1.66	1.15	0.87	1.49			30.15	96.76
	Aidoudi	AYD2	51.35	19.15	7.72	0.57	2.19	1.72	1.41		0.94	0.02	14.30	99.37
Jurassic	J. Ressas	RC4	29.81	10.38	3.86	26.90	0.86		1.51				24.90	98.22
	J. Ben Younes	JRB1	48.85	19.00	6.72	7.90	1.69	0.70	3.85	0.00			10.25	98.96
	J. Lansarine	L1	53.14	12.65	8.15	4.62	4.48	0.43	3.62	0.35		0.01	12.05	99.50
	J. Oust	OS1	50.41	16.80	6.72	8.68	1.36	0.67	3.74	0.25		0.01	10.94	99.58
	Zaghouan	PO8a	47.06	12.85	3.43	12.88	1.23	0.16	4.82	0.00			16.59	99.02
	Zaghouan	PO14	30.74	10.12	3.86	26.52	1.19	0.04	2.46	0.59			24.12	99.64
	J. Zerras	ZR163a	34.94	14.34	5.00	18.34	1.21	0.15	4.16	0.57			20.15	98.86
	J. B Saïdane	BS9	34.92	8.94	2.86	24.92	0.80	0.09	2.65	0.00			23.10	98.28
Triassic	J. Ouest	TJO1	58.16	14.87	6.25	2.67	3.90	0.43	4.04	1.63	0.22		7.48	99.65
	Mateur	TCH1	55.55	17.25	6.93	0.55	3.81	0.30	6.02	0.35	0.37		7.47	98.60
	Lansarin	TJD1	58.26	16.16	6.00	1.15	4.47	0.11	6.38	0.47	0.23		6.10	99.33
	J. Ressas	TJR1	49.63	18.10	7.86	4.20	5.79	0.40	5.18	0.33		0.01	8.17	99.67
	J. Ammar	TAM2	27.10	9.26	4.46	25.64	1.91	0.17	3.65	1.72	0.20		23.99	98.10
	Jalta	TJOM1	48.21	21.17	9.09	0.43	6.63	0.15	7.03	0.31	0.33		5.40	98.75
	Borj Adouani	TBA1	51.42	19.45	10.72	1.26	2.07	1.75	4.22	0.42		0.01	8.44	99.76
Permian–Triassic	Hirech	SP5	72.91	12.68	4.14	0.18	0.34	0.54	4.22			0.03	2.76	97.80
Late Permian	Oil drilling LG2	PRM3	43.86	16.63	6.60	3.90	3.15	1.70	3.13	5.88			14.63	99.48
Permian	Dkilet Toujane	Pr1	40.93	16.18	9.29	6.02	2.29	0.49	4.10	6.70		0.01	13.61	99.62
Early Devonian	Oil drilling MG1	DV2	55.34	20.78	6.00	2.25	1.11	0.84	2.77	1.06			9.15	99.30
Cambrian–Ordovician	Oil drilling BMT1	ORD1	61.98	18.72	5.58	0.17	1.28	0.88	5.78	0.00			3.26	97.65

[a]Decrée *et al.* (2014).
[b]Garnit *et al.* (2017).
LOI = loss on ignition.

calculating regressions between *REE*s and the mineralogical components of mono-mineral samples are dominant in illite, followed by mixed-layer illite-smectite, palygorskite, Mg-smectite, sepiolite and carbonates. The Palaeozoic, Triassic and Jurassic horizons rich in illite are most enriched in *REE*s. Moreover, the horizons with palygorskite in the continental Eocene are poorer in *REE*s, while the halloysite-rich horizons have the lowest *REE* contents (Fig. 4 & Table 4).

The *REE* distribution curves are very comparable and there are no significant changes in *REE* associations (Fig. 4). Moreover, the sample from the Permo-Triassic of Hirech in the Northern Atlas exhibits considerable depletion of heavy *REE*s probably due to slight metamorphism. Similarly, the horizons rich in halloysites display a slight depletion of *REE*s, demonstrating the lower affinity of halloysites for *REE*s compared to other clay minerals.

Three phosphate samples richer in *REE*s compared to the remaining studied samples were extracted from the phosphate mines of Kef Eddour, Jebel (J.) Jebes and Sraa Ourten (Garnit *et al.*, 2017). The *REE* concentrations at Sraa Ourten and J. Jebes are lower than those in Kef Eddour because of the lower level of P_2O_5, which is responsible for *REE* retention. This result was confirmed by Garnit *et al.* (2017), who suggested that Fe-Mn oxyhydroxides play an important role in hosting *REE*s in the Metlaoui Basin (Kef Eddour). Moreover, phosphate samples exhibit a negative anomaly in Ce, confirming the marine origin of these deposits (Fig. 4). In addition, the abundance of *REE*s the Oued Bélif belt breccia (Decrée *et al.*, 2014) and in its rhyodacite alteration products (Badurina & Šegvić, 2022) was also observed in the current study.

All samples are rich in light *REE*s (*LREE*s), except for Ain Khmouda's halloysite, which has a large heavy *REE* (*HREE*) content, suggesting a greater affinity of halloysite to *HREE*s than other minerals. In addition, it is clear that trace elements (Fig. 5) in Jebel Ammar (TAM2) and Jebel Ressas (RC4) have great *REE* concentrations due to their proximity to mineralization zones. The greatest concentration of trace elements (7000 ppm) was detected at Jebel Ammar

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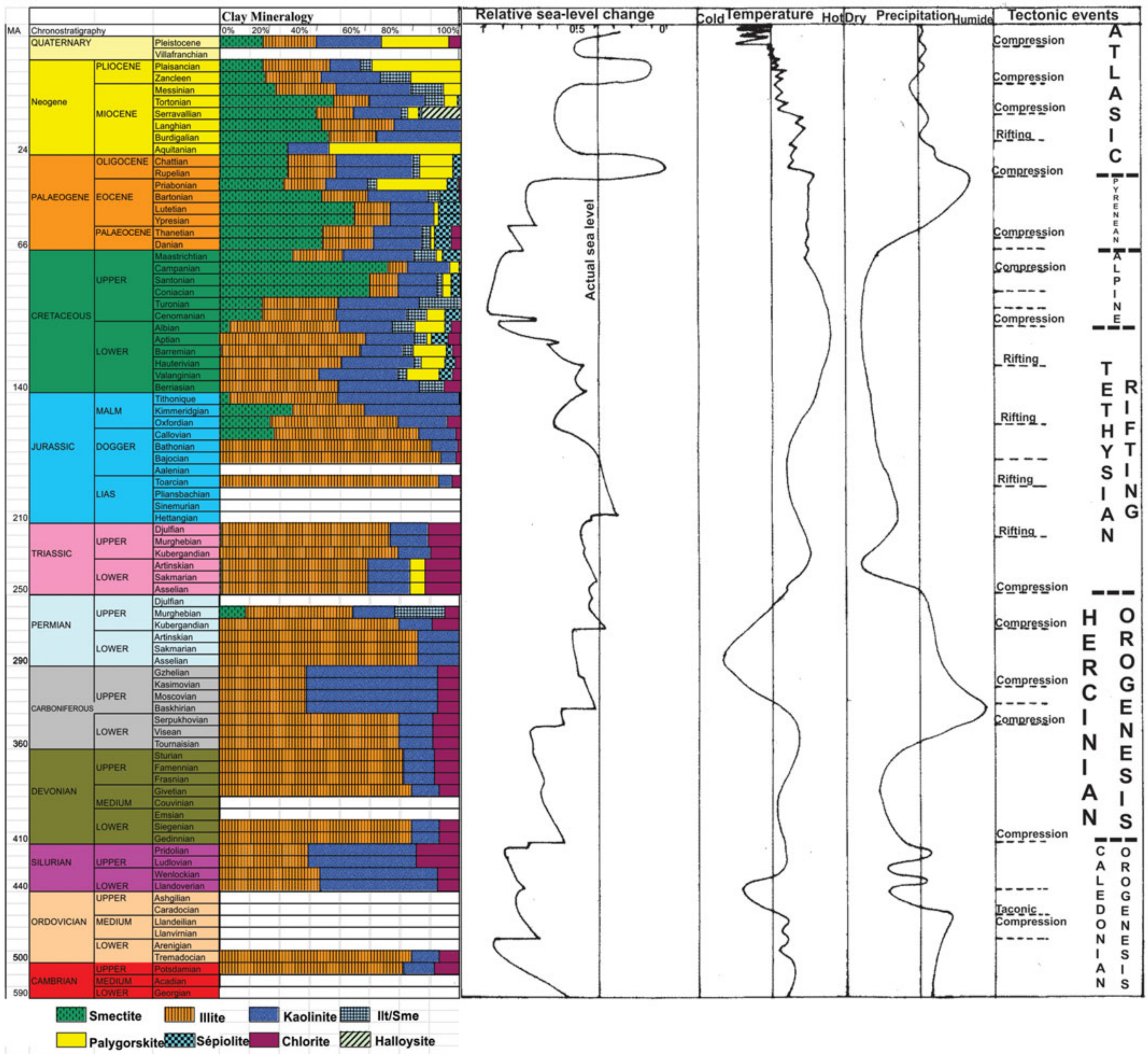

Fig. 2. Clay mineralogy, eustatism, temperature, precipitation and tectonic relationships in the study area (modified from Jamoussi *et al.*, 2003). Ilt/Sme = illite/smectite.

(TAM2; Fig. 5). The greatest *REE* content of the phosphate sample (KCEI) coincides with a relatively large trace element content. This observation should be considered in future studies or exploitations of these *REE*s. Finally, the large *REE* concentration in the altered rhyodacite horizons of Oued Bélif is accompanied by an increase in the abundance of trace elements (Fig. 5).

Influence of tectonic and climate eustatism on *REE*s

The Tunisian margin can be subdivided into six palaeogeographical and geological domains from the 'Saharan Platform' in the south to the 'Nappes Zone' in the north (Fig. 1). These tectono-palaeogeographical domains were established after seven successive geodynamic events that can be summarized as follows (Fig. 2):

(1) Caledonian and Hercynian orogenesis in the Devonian–Silurian and Permian (Bédir *et al.*, 2001);
(2) Tethyan rifting in the Jurassic, Triassic and lower Cretaceous (Bédir *et al.*, 2001);
(3) Alpine orogenesis of the Austrian phase;
(4) Early Pyrenean orogenesis in the uppermost Cretaceous;
(5) Late Pyrenean orogenesis in the Palaeocene–Eocene;
(6) Rifting from the Middle Miocene to the Langhian;
(7) Alpine and Atlasic orogenesis of the upper Miocene and Quaternary.

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Table 2. Mineralogical analysis (%) of the levels studied.

Age	Site	Sample	Sme	Ilt	Kln	Ilt/Sme	Plg	Sep	Chl	Hly	Cal	Dol	Qtz	Gp	Kfs
Miocene	Oued Bélif	OAr4[a]													
Pliocene	Menzel Temime	ACBL	26	40	21	0	0	0	0	0	2	0	10	1	0
Miocene	Aïn Khmouda	AK9	0	0	0	0	0	0	0	100	0	0	0	0	0
	Tamra	HT	0	0	0	0	0	0	0	100	0	0	0	0	0
Eocene	J. Lessouda	JLS3	1	13	3	0	50	0	1	0	0	29	0	0	3
	J. Rhéouis	JRHA6	0	2	0	0	17	0	0	0	0	80	1	0	0
	J. Rhéouis	JRH2	0	0	0	0	36	0	0	0	0	62	1	0	1
	J. Rhéouis	JRH6	0	0	0	2	33	0	0	0	0	62	1	0	2
	J. Bouloufa	BOL5	1	1	1	1	12	0	0	0	58	0	20	0	6
	J. Hamri	HM3	0	0	0	0	3	0	0	0	28	0	65	0	4
Palaeocene–Eocene	Sraa Ouertene	SRO1[a]													
	J. Jeebs	JBS4[a]													
	Kef Eddour	KECI[a]													
Campanian–Maastrichtian	J. Orbata	K34	43	38	4	0	3	1	0	0	4	0	4	2	1
	J. Stah	T23	55	3	14	0	2	1	0	0	14	0	9	0	2
	J. Stah	T24	58	5	3	0	3	1	0	0	3	10	17	0	0
Campanian	Chaouech	GL9	31	3	4	0	0	0	0	0	59	0	3	0	0
	Chaouech	GL11	29	4	4	0	0	0	0	0	60	0	3	0	0
	J. Orbata	K19	44	0	6	0	0	0	0	0	47	0	3	0	0
Coniacian–Santonian	O. Louh Zeflana	Z8	0	7	4	5	0	7	0	0	71	0	6	0	0
	J. Oust	M4	27	6	9	0	0	0	0	0	47	0	11	0	0
	J. Stah	T6	16	3	6	0	2	1	0	0	62	7	3	0	0
	Aidoudi	AYD2	81	3	9	0	0	0	0	0	0	0	6	0	1
Jurassic	J. Ressas	RC4	0	17	8	11	15	0	0	0	37	0	12	0	0
	J. Ben Younes	JRB1	9	27	40	0	0	0	0	0	3	0	18	0	3
	J. Lansarine	L1	0	44	7	0	0	0	9	0	0	10	30	0	0
	J. Oust	OS1	17	8	14	0	0	0	6	0	21	0	31	0	3
	Zaghouan	PO8a	0	51	0	0	0	0	0	0	36	0	12	0	1
	Zaghouan	PO14	0	41	0	0	0	0	2	0	42	0	15	0	0
	J. Zerras	ZR163a	0	61	0	0	0	0	6	0	13	0	19	0	1
	J. B Saïdane	BS9	0	40	0	0	0	0	3	0	34	0	22	0	1
Triassic	J. Ouest	TJO1	0	69	3	0	0	0	4	0	0	3	21	0	1
	Mateur	TCH1	0	66	4	0	0	0	4	0	0	0	26	0	0
	Lansarin	TJD1	0	63	8	0	0	0	7	0	0	0	22	0	0
	J. Ressas	TJR1	0	37	27	0	0	0	3	0	6	0	25	0	2
	J. Ammar	TAM2	2	14	4	0	0	13	2	0	40	0	17	0	9
	Jalta	TJOM1	0	46	24	0	0	0	21	0	0	0	9	0	0
	Borj Adouani	TBA1	0	39	20	0	0	0	25	0	0	0	13	0	3
Permian–Triassic	Hirech	SP5	0	55	2	0	0	0	0	0	0	0	36	0	7
Late Permian	Oil drilling LG2	PRM3	0	43	9	0	0	0	13	0	9	2	20	0	4
Permian	Dkilet Toujane	Pr1	0	46	10	15	0	0	9	0	2	0	7	10	1
Early Devonian	Oil drilling MG1	DV2	0	17	21	0	0	0	7	0	1	1	52	0	1
Cambrian–Ordovician	Oil drilling BMT1	ORD1	0	26	4	0	0	0	4	0	1	1	46	0	18

Sme = smectite; Ilt = illite; Kln = kaolinite; Ilt/Sme = interstratified illite/smectite; Plg = palygorskite; Sep = sepiolite; Chl = chlorite; Hly = halloysite; Cal = calcite; Dol = dolomite; Qtz = quartz; Gp = gypsum; Kfs = K-feldspar.
[a]Decrée *et al.* (2014).
[b]Garnit *et al.* (2017).

It has been proposed that the decline in sea levels and intensification of erosion from the Palaeozoic to the lower Cretaceous is responsible for the large inflow of illite and kaolinite in the area (Jamoussi, 2001; Jamoussi *et al.*, 2003). The mineralogical variations of the Palaeozoic are probably caused by the various orogeneses, because the climate can affect the clay sedimentation only during periods of tectonic stability. The presence of chlorite in Palaeozoic and Triassic sediments is due to diagenetic influences (Deconinck *et al.*, 1985). In addition, the high humidity during the Carboniferous may be the source of the kaolinite abundance, whereas the warm climate during the Late Cretaceous and Palaeogene favoured the formation of the Al-Fe-beidellites that characterize periods of high sea levels (Chamley *et al.*, 1990). The correspondence between the increase in smectite abundance and the maximum flood period is consistent with the decrease in the intensity of erosion resulting from higher sea levels (Fig. 3). The lowering of the sea level during the upper Eocene–Oligocene and Pliocene promoted the formation of closed basins, which induced the formation of palygorskite at high pH and with an intake of Mg (Jamoussi *et al.*, 2003).

Thus, it can be concluded that the Palaeozoic clays were produced by the alteration of the crystalline basement rocks (Jamoussi, 2001). However, the deposits of the Triassic and Jurassic were formed by clastic clays and neoformed palygorskite. The upper Cretaceous smectites are the result of underwater alteration of volcanic material, a pedogenic process and tectonic stability. Furthermore, continental Eocene deposits combine the neoformation and transformation of older materials. However, the Miocene halloysite deposits were neoformed (Jamoussi *et al.*, 2003).

These results show that the mineralogical compositions of sediments and, therefore, *REE*s are influenced by sea-level variations, phases of tectonic activity and palaeoclimate. It is also clear that the increases in the eustatic level were accompanied by increased abundances of smectite, while the abundance of the palygorskite coincides with the lowering of the sea level (which would be linked in Tunisia to the Austrian, Pyrenean,

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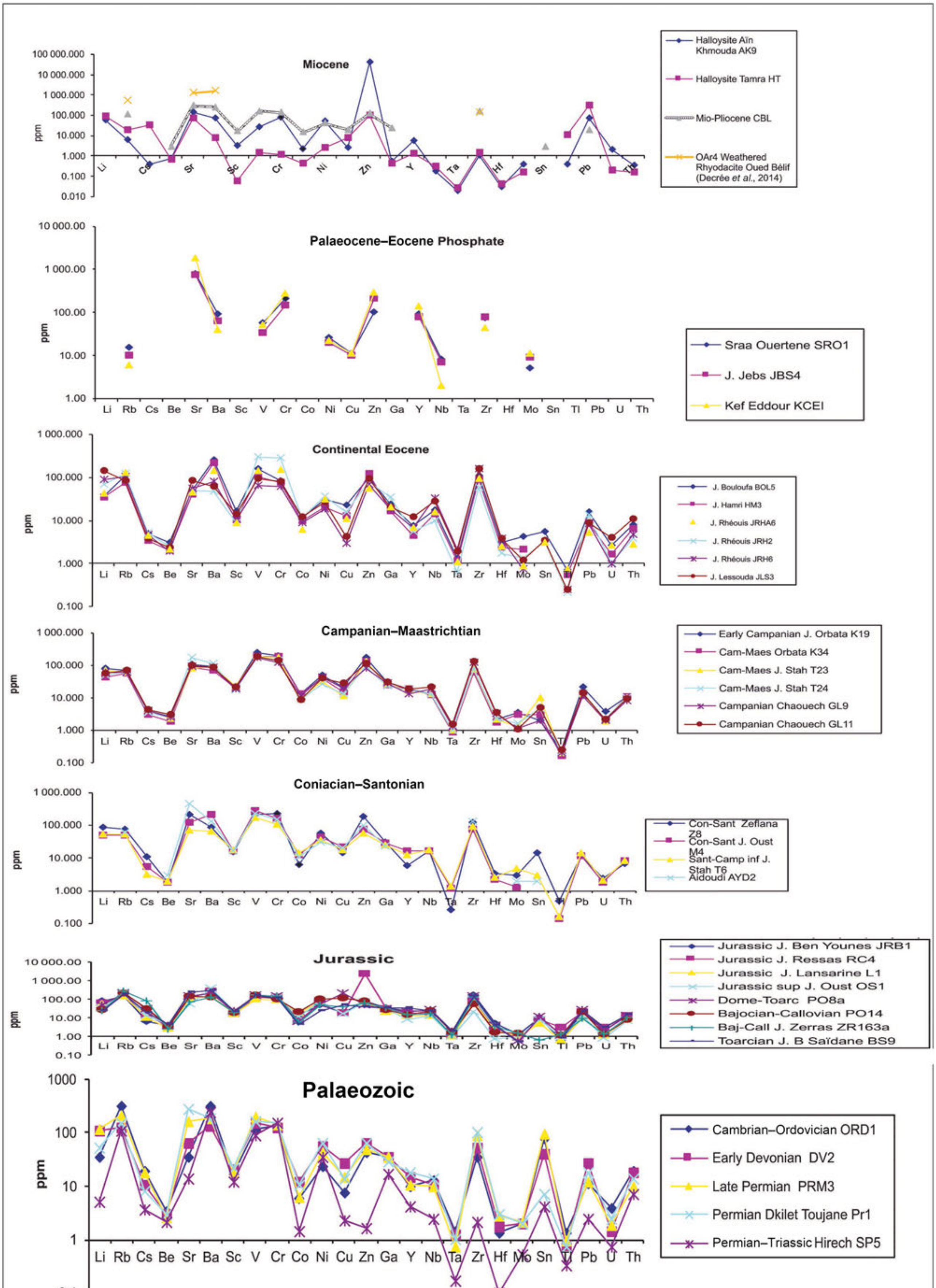

Fig. 3. Distribution curves of the trace elements of the clays from the stratigraphic series studied.

Table 3. Chemical analysis of the trace elements (ppm) from the levels studied.

Age	Site	Sample	Li	Rb	Cs	Be	Sr	Ba	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Y	Nb	Ta	Zr	Hf	Mo	Sn	Tl	Pb	U	Th
Miocene	Oued Bélif	OAr4[a]		530.00			1289.00	1581.00										16.4	1.25	138	4.05					4,46	21,16
Pliocene	Menzel Temime	CBL		119.00	11.70	3.00	292.00	250.00	17.00	165.00	140.00	15.00	40.00	20.00	120.00	25	27.4	16.5	1.35	166	4.3		3	0.23	20	2.83	13.9
Miocene	Aïn Khmouda	AK9	58.46	6.34	0.39	0.74	136.68	74.26	3.37	25.14	84.02	2.23	52.21	2.58	4.33E+04	0.53	5.82	0.17	0.02	1.09	0.03	0.39	0.00	0.39	70.46	2.10	0.34
	Tamra	HT	91.98	18.02	31.80	0.67	72.95	8.05	0.06	1.52	1.24	0.43	2.50	8.18	97.68	0.42	1.28	0.31	0.03	1.40	0.04	0.16	0.00	11.36	307.91	0.19	0.16
Eocene	J. Lessouda	JLS3	138.40	82.72	3.77	2.40	85.86	62.07	13.85	94.09	80.36	12.16	26.69	4.18	95.53	20.69	12.09	27.24	1.94	156.00	3.89	1.18	3.49	0.25	8.96	4.09	10.77
	J. Rhéouis	JRHA6	43.49	128.36	4.39	2.12	44.45	143.86	8.75	139.31	150.57	6.09	30.40	10.75	53.98	20.04	6.76	15.35	1.08	92.79	2.54	0.86	3.03	0.73	5.12	2.59	2.79
	J. Rhéouis	JRH2	68.97	123.27	5.29	2.43	48.59	46.36	9.01	301.97	275.38	11.13	36.56	15.92	78.89	34.18	5.34	9.56	0.63	59.16	1.71	1.35	3.21	0.22	13.70	1.01	3.88
	J. Rhéouis	JRH6	88.62	102.83	4.56	1.87	55.20	78.06	10.29	65.25	62.60	8.97	18.54	2.92	69.50	18.15	6.64	31.89	2.16	159.94	3.81	0.73	0.00	0.25	8.12	0.98	4.66
	J. Bouloufa	BOL5	36.46	107.94	5.02	3.11	49.84	246.87	16.74	161.00	85.11	11.51	31.77	22.83	98.29	24.40	7.61	17.14	1.35	107.01	3.01	4.14	5.55	0.72	16.01	2.57	7.96
	J. Hamri	HM3	35.27	75.67	3.37	2.00	40.27	212.50	11.02	102.72	77.38	9.85	19.87	12.95	123.24	16.38	4.40	14.39	1.10	89.38	2.33	2.08	0.00	0.55	8.59	1.61	6.40
Palaeocene–Eocene	Sraa Ouertene	SRO1[b]		15.00			783.00	92.00	4.40	58.00	214.00		26.00	11.00	99.00		91.00	8.00		74.00	1.50	5.00				19.30	4.30
	J. Jeebs	JBS4[b]		10.00			753.00	64.00	3.40	33.00	149.00		20.00	10.00	210.00		77.00	7.00		76.00	1.60	9.00				17.40	5.10
	Kef Eddour	KCEI[b]		6.00			1820.00	40.00	5.10	52.00	273.00		22.00	11.00	290.00		140.00	2.00		44.00	0.60	11.00				34.20	14.10
Campanian–Maastrichtian	J. Orbata	K34	43.76	56.78	2.95	1.81	84.67	69.59	19.69	176.54	177.65	13.41	39.47	15.11	131.11	24.41	18.29	11.97	0.85	60.78	1.76	3.05	3.04	0.17	14.20	2.11	10.49
	J. Stah	T23	71.05	58.34	4.04	2.33	80.47	91.41	22.14	185.93	167.96	9.33	32.61	11.51	128.74	26.73	15.75	13.50	0.98	75.82	2.13	1.31	9.97	0.20	13.22	1.88	9.66
	J. Stah	T24	49.64	62.62	3.41	2.39	165.40	114.71	17.29	175.37	136.49	8.35	26.68	12.96	91.13	22.95	16.92	13.01	0.98	77.74	2.23	1.63	4.57	0.22	13.72	2.37	9.69
Campanian	Chaouech	GL9	58.44	61.40	3.90	2.45	93.76	85.24	18.68	166.53	119.44	11.26	41.14	20.00	81.75	27.33	13.44	18.24	1.36	118.27	3.20	1.16	2.04	0.20	11.48	1.95	7.86
	Chaouech	GL11	55.48	69.96	4.36	2.97	98.79	87.75	21.39	188.87	140.85	8.57	40.70	27.62	109.50	29.05	18.29	21.21	1.47	132.27	3.55	1.10	4.86	0.25	14.22	2.15	9.42
	J. Orbata	K19	78.51	71.16	3.91	2.56	108.49	92.34	21.70	238.57	191.24	12.60	49.48	21.68	171.55	29.20	18.64	13.31	1.01	72.30	2.17	3.54	1.94	0.24	21.32	3.72	10.52
Coniacian–Santonian	O. Louh Zeflana	Z8	87.71	75.238	11.14	1.82	207.28	84.85	15.06	212.05	220.40	6.13	55.41	14.80	186.09	31.76	5.87	16.11	0.25	120.30	3.31	2.89	14.47	0.48	11.99	2.34	6.60
	J. Oust	M4	50.67	49.44	5.44	1.79	122.91	218.34	16.40	282.88	162.08	12.56	42.13	21.67	76.69	27.99	17.03	16.44	1.21	78.09	2.27	1.28	0.00	0.14	11.63	1.79	8.46
	J. Stah	T6	51.71	52.64	3.06	1.94	71.58	63.62	17.84	169.65	107.54	14.68	36.25	17.22	56.76	25.70	12.33	17.56	1.33	93.84	2.54	4.85	3.01	0.16	14.45	2.03	8.46
	Aidoudi	AYD2		62.00	9.60	3.00	443.00	134.00	17.00	225.00	150.00	11.00	30.00	20.00	100.00	23.00	23.80	11.20		134.00		2.00	2.00				
Jurassic	J. Ressas	RC4	66.61	166.88	14.31	3.40	113.93	276.14	17.85	139.46	131.86	7.06	61.97	19.04	2387.17	30.92	19.22	16.80	1.20	85.02	2.46	0.95	8.57	2.96	22.73	3.19	13.53
	J. Ben Younes	JRB1	83.09	153.81	6.58	3.81	155.28	218.77	22.55	131.79	121.31	14.61	48.63	17.97	78.00	33.12	25.08	25.38	1.93	163.32	4.89	1.33	10.35	0.62	19.74	2.14	13.46
	J. Lansarine	L1	59.33	147.92	10.10	2.69	114.42	141.13	17.36	107.56	88.40	19.32	74.00	0.00	71.92	21.40	12.73	13.72	0.99	68.36	2.09	1.01	5.22	0.65	10.37	1.22	8.16
	J. Oust	OS1	36.92	227.32	13.42	4.27	56.66	377.56	20.76	160.44	126.39	12.29	82.25	16.71	74.07	31.47	7.75	14.03	1.10	20.29	0.73	1.08	7.95	0.99	13.71	0.83	7.05
	Zaghouan	PO8a	48.33	209.77	30.08	4.05	145.48	211.07	22.86	171.34	144.90	6.33	59.39	208.37	49.65	32.28	22.51	26.10	1.97	143.52	4.05	0.61	11.36	1.12	27.26	2.23	13.69
	Zaghouan	PO14	28.68	202.10	29.44	3.72	142.37	129.86	20.16	171.81	104.95	21.13	107.64	111.77	84.71	26.96	14.93	23.29	1.71	55.92	1.79	1.47	0.00	1.16	22.38	1.30	8.00
	J. Zerras	ZR163a	23.11	263.27	80.19	2.56	69.45	131.73	18.45	175.60	148.11	5.65	49.64	40.14	62.53	34.38	15.31	17.14	1.16	129.88	3.48	1.59	0.64	1.39	9.14	1.37	9.85
	J. B Saïdane	BS9	23.19	185.37	19.41	4.32	235.97	308.47	20.71	172.76	119.52	4.51	25.21	49.92	38.81	34.52	33.45	24.69	1.92	142.61	3.95	0.48	0.00	0.79	25.40	3.23	15.09
Triassic	J. Ouest	TJO1	78.36	174.20	8.41	3.22	1324.83	458.26	22.45	154.72	117.85	9.10	34.40	14.49	52.92	28.08	17.18	10.37	0.76	89.16	2.75	0.42	3.46	0.54	6.55	2.46	10.58
	Mateur	TCH1	60.36	159.13	6.58	2.95	536.95	204.15	27.67	153.38	140.26	8.42	40.79	5.84	53.10	27.58	11.54	11.42	0.81	79.32	2.35	0.46	8.13	0.43	19.10	2.24	10.61
	Lansarin	TJD1	80.11	173.23	7.72	3.43	1309.21	423.98	22.01	148.14	103.62	8.87	27.46	8.73	68.17	27.98	7.89	6.40	0.59	47.96	1.66	0.63	4.77	0.47	4.62	2.11	9.29
	J. Ressas	TJR1	91.41	139.40	5.51	3.19	112.91	217.11	24.09	158.22	114.51	10.32	50.54	36.90	83.80	32.06	25.45	23.24	1.75	155.66	4.22	1.80	0.00	0.50	16.77	1.98	11.40
	J. Ammar	TAM2	74.00	115.49	11.20	1.89	4359.55	251.47	3.89	145.75	141.31	7.08	53.56	20.29	1411.66	31.27	7.92	6.70	0.41	19.94	0.49	4.80	0.00	0.58	213.24	1.46	4.50
	Jalta	TJOM1	70.96	228.76	6.36	6.40	11.39	134.98	26.87	186.43	127.60	3.43	52.18	2.20	10.11	37.31	3.83	2.82	0.34	29.59	1.08	0.88	10.52	0.44	1.72	2.16	3.32
	Borj Adouani	TBA1	92.91	171.36	5.57	3.04	105.83	379.18	22.41	112.68	100.88	26.34	86.27	43.82	81.85	21.87	31.83	5.52	0.42	52.70	1.54	11.46	0.00	0.73	33.18	3.16	8.23
Permian–Triassic	Hirech	SP5	5.29	108.24	3.68	2.16	13.75	253.09	12.14	91.49	150.42	1.43	34.91	2.26	1.71	17.67	4.18	2.56	0.17	2.17	0.10	0.55	4.12	0.33	2.44	0.73	7.04
Late Permian	OildrillingLG2	PRM3	118.23	217.22	17.88	2.60	167.39	191.27	18.65	200.50	148.80	6.43	42.78	14.50	48.65	35.92	10.53	9.83	0.73	89.85	2.77	2.19	94.20	0.98	12.51	1.93	
Permian	Dkilet Toujane	Pr1	54.03	151.10	8.12	3.09	271.99	190.09	22.23	164.77	149.61	10.69	66.39	13.63	65.10	28.39	18.21	13.81	1.03	103.94	3.12	1.96	7.18	0.74	18.41	2.42	14.35
Early Devonian	OildrillingMG1	DV2	110.96	129.08	10.92	2.93	65.41	137.86	20.25	151.10	129.52	12.02	54.92	26.63	65.15	35.54	15.35	10.46	1.28	51.46	1.73	2.02	39.87	0.79	27.85	1.50	17.78
Cambrian–Ordovician	OildrillingBMT1	ORD1	34.48	329.97	19.40	3.57	34.52	316.02	17.26	114.65	134.55	5.75	24.03	7.61	43.81	35.18	10.05	12.91	1.47	34.87	1.39	1.97	80.47	1.36	11.24	3.97	19.78

[a]Decrée *et al.* (2014).
[b]Garnit *et al.* (2017).

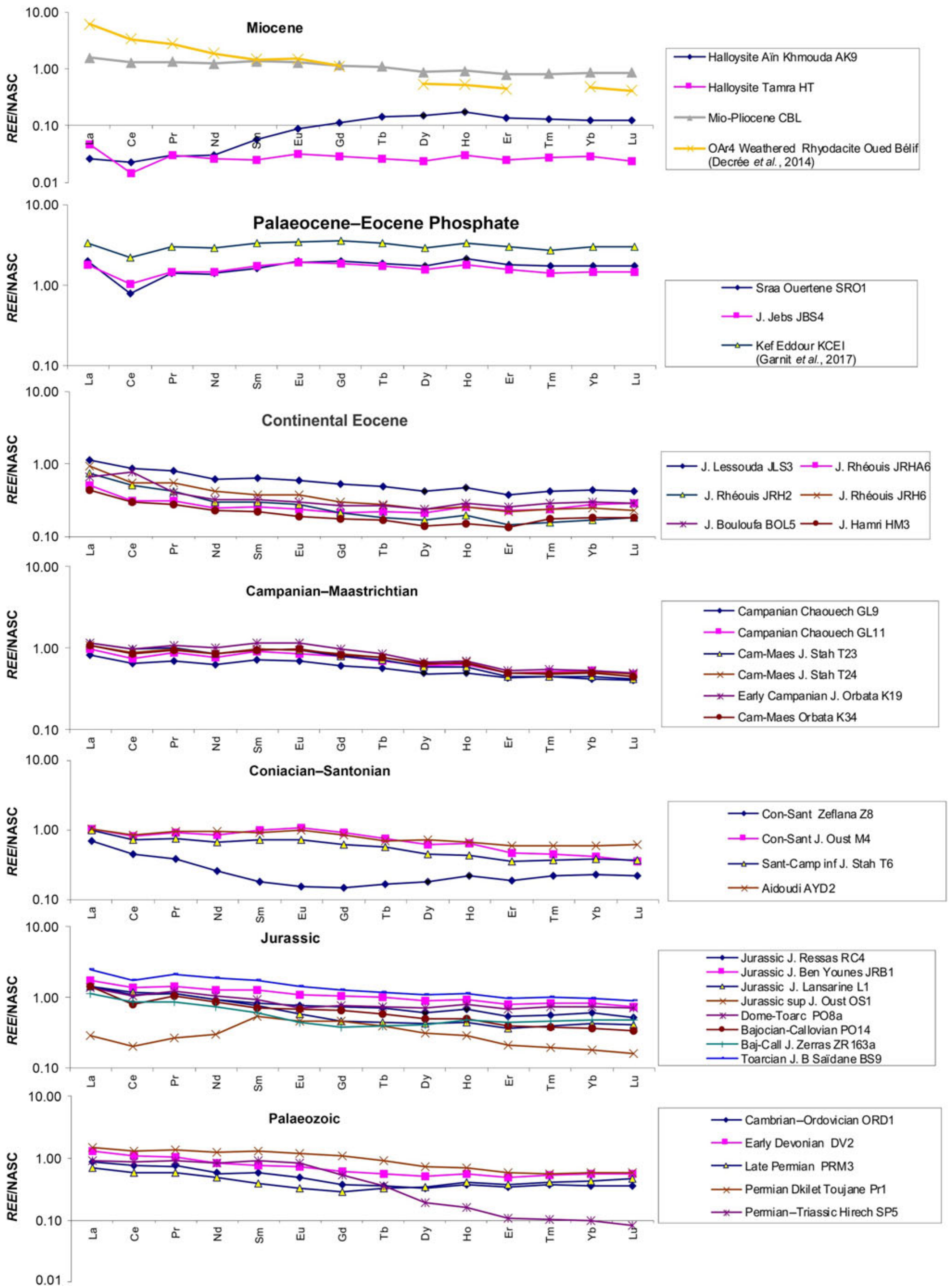

Fig. 4. Normalized *REE* patterns of clays in the studied stratigraphic series.

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Table 4. Chemical analysis of REEs (ppm) from the levels studied.

Age	Site	Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑*REE*
Miocene	Oued Bélif	OAr4[a]	183.00	244.00	21.60	61.20	8.33	1.87	5.87		2.96	0.55	1.50		1.49	0.20	532.57
Pliocene	Menzel Temime	CBL	47.50	95.40	10.50	40.60	7.68	1.59	5.97	0.92	4.85	0.96	2.71	0.41	2.63	0.41	222.13
Miocene	Aïn Khmouda	AK9	0.77	1.64	0.23	0.98	0.33	0.11	0.58	0.12	0.82	0.18	0.47	0.06	0.39	0.06	6.76
	Tamra	HT	1.40	1.04	0.23	0.86	0.14	0.04	0.15	0.02	0.13	0.03	0.08	0.01	0.09	0.01	4.24
Eocene	J. Lessouda	JLS3	34.13	62.45	6.24	20.53	3.62	0.72	2.76	0.42	2.33	0.48	1.26	0.21	1.37	0.20	136.71
	J. Rhéouis	JRHA6	16.44	22.66	2.41	8.28	1.44	0.30	1.11	0.19	1.17	0.26	0.77	0.12	0.86	0.14	56.13
	J. Rhéouis	JRH2	23.82	37.66	3.27	9.82	1.72	0.35	1.11	0.16	0.93	0.20	0.50	0.08	0.53	0.09	80.23
	J. Rhéouis	JRH6	27.53	40.38	4.26	13.94	2.16	0.46	1.56	0.24	1.31	0.27	0.74	0.12	0.76	0.11	93.83
	J. Bouloufa	BOL5	19.68	56.66	3.25	10.53	1.86	0.37	1.37	0.22	1.31	0.30	0.88	0.14	0.91	0.14	97.63
	J. Hamri	HM3	13.08	22.12	2.23	7.49	1.26	0.24	0.90	0.14	0.76	0.16	0.47	0.09	0.56	0.09	49.56
Palaeocene–Eocene	Sraa Ouertene	SRO1[b]	59.20	57.80	11.30	46.80	9.40	2.45	10.30	1.60	9.70	2.20	6.20	0.86	5.40	0.84	224.05
	J. Jeebs	JBS4[b]	57.20	76.70	11.80	49.20	9.80	2.37	9.80	1.50	8.60	1.90	5.30	0.72	4.60	0.70	240.19
	Kef Eddour	KCEI[b]	108.00	164.00	23.50	96.50	18.90	4.34	18.40	2.80	16.10	3.50	10.10	1.38	9.20	1.46	478.18
Campanian–Maastrichtian	J. Orbata	K34	32.06	63.15	7.52	28.49	5.43	1.21	4.36	0.66	3.63	0.69	1.70	0.24	1.57	0.22	150.92
	J. Stah	T23	35.21	71.37	8.07	28.53	5.54	1.16	4.23	0.61	3.24	0.62	1.51	0.23	1.37	0.20	161.91
	J. Stah	T24	32.54	65.75	7.79	28.60	5.66	1.18	4.52	0.65	3.42	0.71	1.68	0.25	1.58	0.23	154.55
Campanian	Chaouech	GL9	25.26	47.46	5.59	21.09	4.09	0.86	3.20	0.49	2.74	0.52	1.47	0.22	1.32	0.20	114.51
	Chaouech	GL11	29.12	55.16	6.92	25.42	5.17	1.08	4.23	0.59	3.34	0.67	1.67	0.26	1.64	0.23	135.49
	J. Orbata	K19	35.08	72.46	8.69	33.05	6.66	1.42	5.10	0.73	3.76	0.73	1.84	0.27	1.65	0.24	171.70
Coniacian–Santonian	O. Louh Zeflana	Z8	21.96	32.58	3.04	8.38	1.04	0.19	0.78	0.14	0.98	0.23	0.65	0.11	0.71	0.11	70.90
	J. Oust	M4	31.45	59.70	7.19	27.39	5.63	1.32	4.78	0.63	3.39	0.67	1.60	0.23	1.30	0.17	145.45
	J. Stah	T6	29.16	52.85	5.97	21.55	4.13	0.91	3.19	0.49	2.44	0.45	1.23	0.18	1.17	0.18	123.89
	Aidoudi	AYD2	31.40	62.30	7.40	30.80	5.30	1.24	4.40	0.60	3.90	0.70	2.00	0.30	1.80	0.30	152.44
Jurassic	J. Ressas	RC4	42.53	81.08	9.07	30.40	4.80	0.95	3.82	0.60	3.32	0.70	1.86	0.28	1.88	0.25	181.53
	J. Ben Younes	JRB1	52.56	102.02	11.58	41.61	7.31	1.37	5.42	0.86	4.90	0.99	2.74	0.41	2.61	0.35	234.74
	J. Lansarine	L1	43.58	85.18	8.90	30.70	4.41	0.72	2.46	0.38	2.33	0.46	1.27	0.20	1.31	0.20	182.09
	J. Oust	OS1	8.55	15.18	2.10	9.90	3.05	0.58	2.41	0.34	1.72	0.30	0.72	0.10	0.56	0.08	45.59
	Zaghouan	PO8a	41.97	78.02	9.70	35.16	5.27	0.87	4.05	0.64	3.88	0.82	2.35	0.36	2.32	0.34	185.76
	Zaghouan	PO14	43.49	57.70	8.21	28.29	4.12	0.84	3.43	0.50	2.77	0.51	1.33	0.19	1.13	0.17	152.68
	J. Zerras	ZR163a	36.07	63.63	6.79	24.27	3.41	0.55	1.98	0.33	2.25	0.51	1.52	0.23	1.50	0.23	143.28
	J. B Saïdane	BS9	75.81	129.98	16.74	61.73	9.87	1.77	6.78	0.99	5.96	1.16	3.28	0.50	3.03	0.43	318.03
Triassic	J. Ouest	TJO1	39.48	75.19	8.57	31.97	5.55	1.06	4.01	0.59	3.06	0.67	1.79	0.30	2.03	0.30	174.57
	Mateur	TCH1	28.00	220.45	6.27	20.23	3.50	0.67	2.50	0.37	2.38	0.51	1.42	0.24	1.49	0.21	288.24
	Lansarin	TJD1	35.01	64.94	7.24	26.04	4.46	0.81	2.55	0.32	1.84	0.38	1.05	0.16	1.02	0.14	145.96
	J. Ressas	TJR1	49.4	100.83	11.30	40.97	7.06	1.51	5.90	0.88	4.53	0.98	2.47	0.39	2.56	0.35	229.13
	J. Ammar	TAM2	123.51	26.84	3.13	11.67	2.41	0.43	1.71	0.27	1.22	0.24	0.70	0.08	0.6	0.06	172.88
	Jalta	TJOM1	5.20	10.68	1.22	4.57	0.87	0.17	0.66	0.12	0.76	0.17	0.48	0.08	0.51	0.07	25.56
	Borj Adouani	TBA1	22.92	48.81	6.55	27.68	9.12	2.39	9.44	1.36	6.81	1.23	2.98	0.42	2.61	0.33	142.65
Permian–Triassic	Hirech	SP5	27.55	62.48	7.31	27.97	5.26	1.03	2.83	0.31	1.06	0.17	0.36	0.05	0.30	0.04	136.71
Late Permian	Oil drilling LG2	PRM3	21.36	42.34	4.61	15.83	2.27	0.41	1.49	0.28	1.86	0.43	1.26	0.21	1.34	0.23	93.92
Permian	Dkilet Toujane	Pr1	45.45	93.38	10.92	40.80	7.55	1.47	5.63	0.78	3.98	0.74	2.00	0.28	1.86	0.28	215.10
Early Devonian	Oil drilling MG1	DV2	38.55	79.76	8.17	27.10	4.45	0.89	3.15	0.47	2.76	0.59	1.66	0.27	1.75	0.27	169.83
Cambrian–Ordovician	Oil drilling BMT1	ORD1	26.76	55.24	5.93	19.37	3.38	0.61	1.94	0.31	1.83	0.39	1.15	0.18	1.10	0.17	118.35

[a]Decrée *et al.* (2014).
[b]Garnit *et al.* (2017).

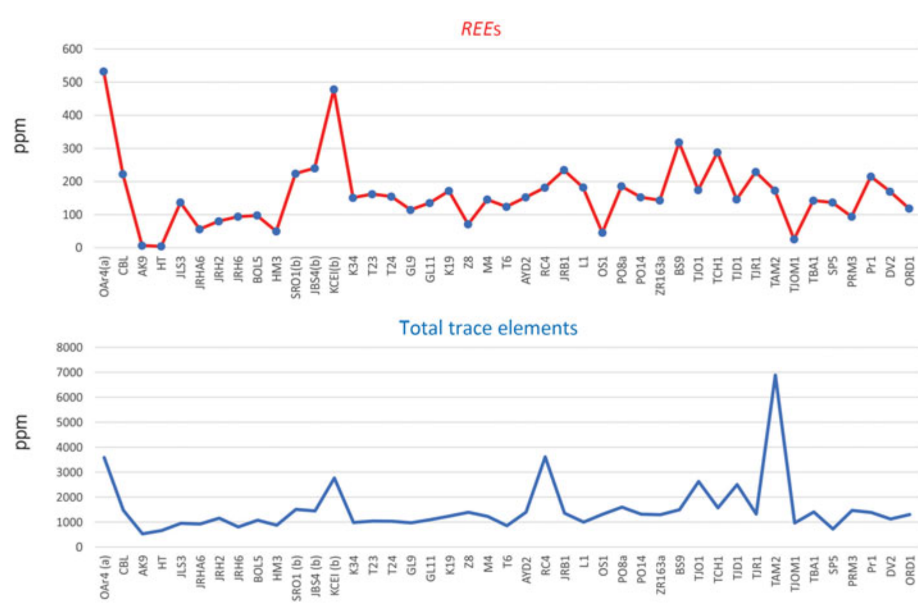

Fig. 5. Comparison of the *REE*s and trace elements of the clays from the stratigraphic series studied. The suffix (a) refers to data from Decrée *et al.* (2014); the suffix (b) refers to data from Garnit *et al.* (2017).

Alpine and Atlasic compressive events) and to the evaporative conditions in the area studied (Jamoussi *et al.*, 2003).

Conclusion

This is the first study to examine the relationship between *REE*s and clay minerals of the stratigraphic series of the Palaeozoic to the Neogene in Tunisia. It provided the following results:

- The *REE* distribution shows limited variability from the Palaeozoic to the Neogene, except during the Triassic, Jurassic and Miocene. The *REE*s did not evolve over time and did not establish equilibrium with the marine environment, which makes them valuable markers of the origins of clay minerals that have not undergone diagenetic modifications.
- The normalized *REE* patterns are most often characteristic of detrital clays such as illite, kaolinite and smectite, which shows that the smectites of the Tunisian margin are mainly continental and probably largely pedogenic.
- Only some fibrous clays have an authigenic origin.
- Illites display the greatest *REE* contents, followed by smectites and palygorskites. The smallest values were recorded in the halloysites.
- Similar to clay minerals, *REE*s are influenced by variations in sea level, phases of tectonic activity and palaeoclimate.
- The phosphate horizons are richer in *REE*s and trace elements compared to the other studied horizons.
- The Oued Bélif belt breccia is rich in *REE*s.
- It is still difficult to evaluate the relative importance of tectonic destabilization, eustatic movements and climatic influence when interpreting the composition and distribution of the *REE*s of the sedimentary column due to the interactions between these three parameters.
- Trace elements are enriched close to mineralization zones.

The industrial exploitation of *REE*s is not possible currently. More work in areas rich in *REE*s will enable the separation of *REE*s from the bulk rock.

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